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**AUTHOR(S):** Cornel Wohlberg and Jerry R. Buchholz

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SILICA IN WATER IN RELATION TO  
COOLING TOWER OPERATION\*

by

Cornel Wohlberg  
Jerry R. Buchholz

H-7, Health Division  
Los Alamos Scientific Laboratory  
University of California  
Los Alamos, New Mexico

INTRODUCTION

A special problem associated with cooling towers in the Los Alamos, New Mexico area is that evaporation concentrates the high (about 80 ppm) initial silica content of the water and causes it to precipitate on heat-exchanger surfaces.

It is common experience at the Los Alamos Scientific Laboratory (LASL) that evaporation of the water in evaporative coolers causes deposition of very hard, although somewhat porous, silica layers that interfere seriously with heat transfer.

Different concentrations are mentioned as being threshold values. No difficulties have been encountered when double the usual concentration (150 ppm or mg/l) is present. At the steam plant, Technical Area sewage effluent to concentrations of 240 ppm of  $\text{SiO}_2$  has been used in condensers with no resultant difficulties.

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The details and purely local factors responsible for deposition will not be considered. The basic factors which may have relevance to the deposition of  $\text{SiO}_2$  at low temperatures will be reviewed.

The assumption on which this work is based is that at some concentration between 150 and 240 ppm of  $\text{SiO}_2$ , especially in the presence of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ , some  $\text{SiO}_2$  will come out of solution. Therefore the "solubility" of silica in its various forms, the nature of the silica molecule or species present, and other factors causing polymerization of such ionic or molecular species will be considered. We have scanned the appropriate fields of relevant geochemical literature. We did not do an exhaustive search. We believe that the literature evaluated will serve as an adequate guide to reconciling seeming contradictions.

At the start, it seemed appropriate to concentrate on methods of removing silica from the water so that only a very little of the incoming water would be blown down; wind and evaporation should cause the major losses.

## DISCUSSION

This discussion will review the nature and solubility of silica. The effects of other ions and factors bearing on the solubility will also be considered.

The silica in the water coming from the wells is dissolved, so most of this review will be concerned with orthosilicic acid,  $\text{Si}(\text{OH})_4$ , and to a much lesser extent with colloidal forms of silica.

### Solubility of Silica

The solubility relationships of the polymorphs of silica such as cristobalite, amorphous silica, and quartz have been well summarized recently (Fig. 1)<sup>1</sup> and Fournier.<sup>2</sup>

Silica "solubility" is a function of the material. Three lower temperature forms, "amorphous silica" (silica gel, pyrolyzed silica, infusorial earth, etc.), cristobalite, and alpha quartz have widely different solubilities at temperatures below about 350°C. The curves shown in Fig. 1 are those proposed by Morey, Fournier, and Rowe,<sup>3</sup> based on earlier work by Lenher and Merrill<sup>4</sup> and others. (For other citations see Barnes.)

The fact that amorphous silica shows a 25°C solubility of about 115 ppm<sup>1,2</sup> (Alexander, et al<sup>5</sup> showed 100-140 ppm at 25°C, a commonly accepted range) contrasted to 3-7 ppm,<sup>1,2,3</sup> for crystal quartz, indicates that different molecular species exist in solution, even if one assumes a much longer period for crystal quartz to come to equilibrium than for amorphous silica to do so.

Figure 2 shows the solubility results of Morey et al<sup>3</sup> and others in somewhat more detail. Figure 3 shows the solubility of different forms of silica as a function of time. Note that the silica gel and supersaturated silica solution approach a similar value, whereas the curves for silica glass show slow solubility with time but rise to higher values. In all likelihood, this is the "very large supersaturation" (Morey et al). According to these data, the silica gel nucleates a polymerization of the soluble

silica so that large supersaturation does not occur. The whole picture is of a metastable system where different conditions and starting materials may cause different dissolved species to appear in solution.

Most writers agree, or postulate, that  $\text{Si(OH)}_4$  is the soluble species and that in solution it is most likely to be present as the monomeric, non-ionized species.

The species measured by the method generally in use since 1947 for "active" silica is the monomeric orthosilicic acid with, possibly, some dimeric acid in solution.<sup>6</sup>

Alexander et al<sup>5</sup> have shown that at least 98% of the monosilicic acid in solution reacts with molybdic acid within 2 min. Their solubility proved to be 140 ppm, as monomeric silica. They equilibrated solutions up to 62 days, but found no substantial change after 20 days. The difference between their results and those of Morey et al<sup>3</sup> is that the latter worked with samples equilibrated up to 1600 days and found substantial changes beyond 100 days. Morey et al also pointed out that the criterion of equilibrium is seldom fulfilled in silica solutions. At equilibrium, the reaction must be reversible to the same solid phase. The solutions actually tend to become very supersaturated, and such supersaturation may last a long time. Slow polymerization may take place, and a variety of polymerized species may form, with eventual formation of colloidal sols and gels.

The solubility of silica seems to be little affected by the ionic strength of the solutions. Siever<sup>7</sup> had found 140 ppm solubility at 25°C in distilled water and similar values in "brines" of 40,000 and 50,000 ppm salt content. Krauskopf<sup>8</sup> had found similar values. Greenberg and Price<sup>9</sup> had found no appreciable effect in solutions of 0.0001 and 0.10 N NaCl and 0.005-0.02 N Na<sub>2</sub>SO<sub>4</sub> solutions. These authors had found the solubility reduced by less than 10% in 1 N sodium chloride solution.

The effect of pH on the solubility of amorphous silica can be illustrated by the work of Alexander et al<sup>5</sup> (Fig. 4). The solubility (at 25°C) is about 140 ppm up to pH 8.5-9. Above 9 it rises rapidly. Since, equilibria are, notoriously, slowly attained in silica solutions, confirmation is supplied by the work of Morey et al<sup>3</sup> who worked with solutions (Fig. 5) from hot springs. The calculated solubility curve can be extended to form an envelope showing solubility vs. pH in solutions standing about 2 yr. The greatest solubility over this period is shown at about pH 1.5. Considerable supersaturation is shown at pH 3.0-3.5 and lower.

One other work should be cited here, as it has a definite bearing both on the origins of silica in water and on the solubility of deposits on heat exchangers. Way and Siffert<sup>10</sup> (Fig. 6) determined short-term silica solubilities of a few species of silica minerals and showed the striking differences between those of "amorphous silica" and "opal" (~10% H<sub>2</sub>O).

The source of the silica and its particle size determine short term or apparent solubilities.<sup>11</sup>

#### The Nature of Silica in Solution

The nature of silica in solution is the key to the problem of removing it. The form in which silica exists in water, whether colloidal, crystalloidal,

or ionic has been the subject of debate.

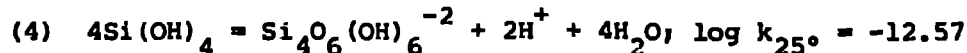
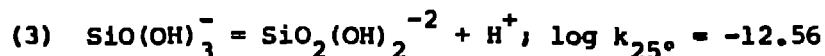
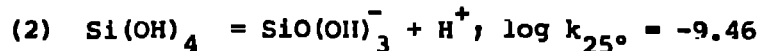
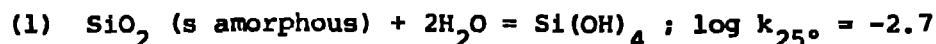
In the earlier geological literature, the silica present in natural waters was assumed to be colloidal. This statement is based in part on Kahlenberg and Lincoln's<sup>12</sup> work and that of Kohlrausch<sup>13</sup> (as quoted by E. S. Moore et al<sup>14</sup>). These earlier workers apparently based their opinions on the hydrolysis of sodium silicates in solution and did not allow enough time for their systems to equilibrate. Nor did they examine natural water critically to determine the nature of the silica present.

Roy<sup>15</sup> examined the data in the chemical literature and found the evidence preponderantly in favor of a true solution of silica in water.

Dienert and Wandenbulte's<sup>16</sup> work, on the colorimetric determination of silica and their differentiation between soluble or crystalloidal and colloidal silica in river water, showed only soluble (no colloidal) silica present. In fact, colloidal silica, at a concentration under the saturation level will dissolve as a function of time and temperature in neutral or alkaline solution. In acid, the conversion is retarded. The colorimetric results are generally comparable to those from gravimetric determination. However, the silica is not in ionic form to an appreciable degree. The first ionization constant, evaluated by Greenberg and Price,<sup>9</sup> is  $10^{-9.77}$ . The solubility and ionization should go up with pH over 9 as previously indicated. Alexander et al<sup>5</sup> also postulated that the dominant species in solution at 25°C and pH 2-8 is  $\text{Si(OH)}_4$ .

Lagerström<sup>17</sup> has made the point that equilibrium, as long as solutions are clear, is instantaneous when working with sodium silicates. Lagerström by the use of precision acid-base titrations, determined equilibria over a wide range of pH values for polymeric and monomeric silica. Stumm et al<sup>18</sup> have recalculated and plotted these results, Fig. 7. .

The silica equilibria plotted are based on the following equations:



in 0.5 molar  $\text{NaClO}_4$  medium.

From the plot it is apparent that the line designated as separating the "mononuclear domain" ( $\log k_{25^\circ} = -2.7$ ) from the "insolubility domain" defines a solubility of 120 ppm up to a pH of about 8.5. At higher pH values there is a stable multimeric domain as indicated by equations 2 and 3, above.

This is good confirmation of the solubility of amorphous silica considering that this is based on potentiometric titrations of sodium silicate solutions in 0.5 molar  $\text{NaClO}_4$ .

For a practical system, this indicates the limit of safe operation in the pH range of 6-8.5 is about 150 ppm.

Fournier<sup>2</sup> showed that in hot spring waters the increase in alkalinity causes the appearance of "cyclic" polymers to appear. These seem to be stable over long periods. O'Connor<sup>19</sup> found previously that the activity of silica present in solution was an inverse function of the  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio. The higher ratios (2-3.5) showing a more polymeric, less reactive (complexed or glassy)  $\text{SiO}_2$ .

The polymers formed at lower pH values are mostly linear (Fournier)<sup>2</sup> and these depolymerize in a matter of minutes. The cyclic polymers require hours.<sup>19</sup>

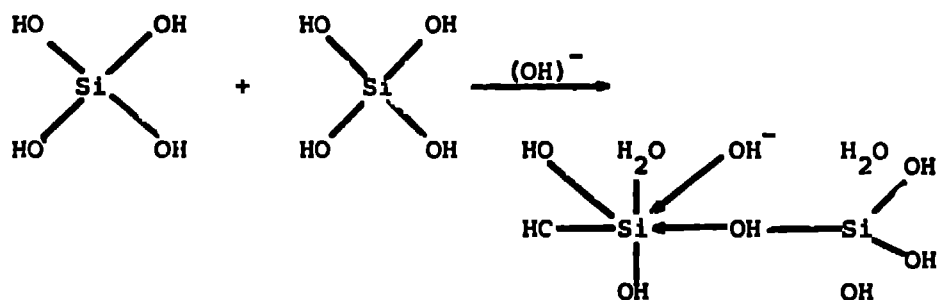
Silica, to be coagulated deliberately, or to precipitate inadvertently, on heat exchangers or other surfaces, must polymerize and become colloidal. The exact conditions causing the initial polymerization may be difficult to



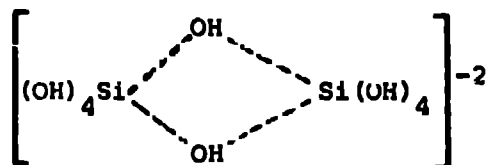
determine; this is the area in which knowledge is scant. However, some of the mechanisms can be examined for clues.

For  $\text{Si}(\text{OH})_4$  to coagulate, Iler<sup>11</sup> (pp. 26-37) postulates that silicon must show a coordination number of 6 instead of the usual 4, quoting Weyl<sup>20</sup> and Treadwell and Wieland<sup>21</sup> who point out that the coordination number of silicon ( $\text{Si}^{++++}$ ) is 6 if the anion is singly charged, is small, or has low polarizability.  $\text{F}^-$  and  $\text{OH}^-$  ions meet these requirements. The two are equivalent in many structures and can replace each other in crystals of large unit cells, such as mica.

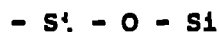
Iler<sup>11</sup> (p. 39) visualized the following reaction sequence.



Alternatively (Iler pp. 46-47), another structure could show hydroxyl bonds linking orthosilicic acids.



The polymerization steps would be followed by dehydration to form:



bonds and further polymerization. Aggregation by Van der Waal's forces leads

to negatively charged sols. Stumm<sup>18</sup> shows that increasing the pH as well as the concentration promotes this process.

Kitahara<sup>22</sup> found that changes in molecular silica concentrations were most rapid at pH 7.5 and slower on both sides of this pH. He further showed that the complex polymerization could be represented as a second-order reaction on the acid side and a third-order equation on the alkaline side. The equation

$$-\frac{dc}{dt} = k(C-C_e)^n$$

was assumed to be applicable,

where C = concentration of molecular silica,

C<sub>e</sub> = concentration at equilibrium,

k = rate constant,

n = order of reaction.

The disappearance of the molecular silica represents the polymerization.

#### Colloidal Silica

The pH range in which colloidal silica is least stable is pH 5.0-8.0 (Fig. 8).<sup>23</sup> The stability of the sol, of course, is a function of the ionic strength. A 100 m M/L solution of NaCl is required to cause gelling of an SiO<sub>2</sub> sol whereas a 15 m M/L BaCl<sub>2</sub> has the same effect.<sup>24</sup>

Colloidal sols of SiO<sub>2</sub> are negatively charged, presumably by adsorbed [H<sub>2</sub>O Si(OH)<sub>5</sub>]<sup>-</sup> ions or hydroxyls in alkaline solutions.<sup>11</sup> Krauskopf<sup>8</sup> (p. 20) found that ferric oxide precipitated in SiO<sub>2</sub> solution removed colloidal SiO<sub>2</sub> but not the dissolved material. Likewise, sea water precipitates colloidal silica, and dissolved supersaturated silica is polymerized and precipitated. However, such precipitation is not immediately complete but "requires several days or weeks to attain a steady state."

The effect of aluminum ion on silica precipitation is well known. Okamoto, Okuna, and Goto<sup>25</sup> found a strongly pH-dependent reaction between silica sols and  $\text{Al}^{+++}$ . One mg/liter of  $\text{Al}^{+++}$  was sufficient to reduce 45 mg/liter of  $\text{SiO}_2$  in the sol to 5 mg/liter in the pH range 4-5 (Fig. 9). As Fig. 10 shows, molecularly dispersed or dissolved silica requires considerably larger ratios of aluminum ion to precipitate the silica. The pH for optimum precipitation is also displaced to 8-9. It seems that  $\text{OH}^-$  ions promote polymerization, as they do depolymerization. Aluminum seems to have an added polymerizing effect, but it certainly shows the coagulating effect of a trivalent ion in increasing the ionic strength and causing coagulation of a negative sol.

One other point might be raised in this connection. Okamoto et al<sup>25</sup> point out that an excess of colloidal silica over alumina keeps both from precipitating (Fig. 11). This is a phenomenon of reversing the charge on the formed alumina sol and thus "protecting" it against precipitation.<sup>26</sup>

#### Precipitation of Silica Under Natural Conditions

Previous discussion has shown that the solubility of amorphous silicas is in the 100-140 ppm range.  $\text{Si}(\text{OH})_4$ ,<sup>1,2,5</sup> a very slightly ionized species,<sup>9,17,27</sup> is generally accepted as the major one in solution.

The role of pH in causing polymerization has been shown (O'Connor,<sup>19</sup> Lagerström,<sup>17</sup> and Stumm,<sup>18</sup>

It has been shown that the solubility of silica is little affected by salts up to 0.2 N.<sup>7,8</sup>

White et al,<sup>28</sup> working with hot-spring waters, found that the silica content of their three most acid waters (pH 5.1-6.1) did not fall below 220 ppm when the water was stored for 120 days at room temperature. Krauskopf<sup>8</sup> found

that solutions at pH less than 7 stayed supersaturated with  $\text{SiO}_2$  much longer than solutions at 7.8 and over. He also showed that partly dehydrated gel hastened the polymerization of dissolved (supersaturated, 332 ppm)  $\text{SiO}_2$ , the higher the pH, the faster the polymerization (pH 7.8 or over). For a solution with 138 ppm  $\text{SiO}_2$  content, the loss of dissolved  $\text{SiO}_2$  was only 5 ppm; whereas, for a 332 ppm solution the loss was 182 ppm in a 35-day period.

White et al<sup>28</sup> agree that supersaturated acid waters and alkaline waters with less than 100% supersaturation tend to remain supersaturated almost indefinitely. Higher temperatures and the presence of opal favor precipitation.

We find other points of similarity among these writers' experiences, natural systems, and the evaporative coolers. Generally, at Los Alamos, precipitation is prevented if the silica is kept below 150 ppm.

#### Clay Formation

The formation and decomposition of clays are relevant to the possible formation of an opaline layer on heat exchangers (more than 60%  $\text{SiO}_2$  and less than 12%  $\text{H}_2\text{O}$ ).

Occasionally, it has been noticed<sup>29</sup> that some of the Los Alamos scale contains what appears to be "tuff dust" (volcanic ash) acting as a nucleus for scale formation. The following discussion may suggest a partial chemical mechanism for such a nucleation conversion of soluble silica to an insoluble opaline layer.

Ocean waters have a maximum silica concentration of 1 to 4 ppm.<sup>30</sup> The temperatures of most of the oceans are 2-5°C, in which case the solubility of quartz would be about 5.7 ppm and that of amorphous silica about 60 ppm. In an attempt to explain this gross undersaturation, MacKenzie and Garrels<sup>31</sup> showed that when some clay minerals, such as kaolinite, glauconite, and montmorillonite, are suspended in sea water enriched in silica (25 ppm) the dissolved silica

decreases rapidly. The clays take up some of the silica. If the water is deficient in  $\text{SiO}_2$  (0.03 ppm), the clays rapidly yield silica to the water.

The significance of this locally may be that wind-borne clay minerals from tuff are caught in water in cooling towers and upon deposition on heat exchangers form a nucleus for silica deposition from the relatively silica-rich (80-150 ppm) water. In this respect, we note that MacKenzie and Garrels also found that a solid hydroxylated magnesium silicate forms when the  $\text{SiO}_2$  concentration exceeds 26 ppm, at pH 8.1.

Wollast<sup>32</sup> calculates that at pH 7.8 sepiolite [ $2\text{MgO} \cdot 3\text{SiO}_2 \cdot 3.5 \text{H}_2\text{O}$ ] will dissolve to the extent of 60 ppm  $\text{SiO}_2$  and at pH 8.5 to the extent of about 6.7 ppm.

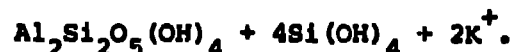
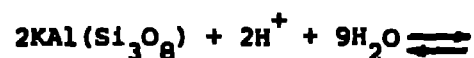
Hem et al<sup>33</sup> have shown that  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , halloysite, an amorphous product related to kaolinite can be formed at pH 4-10 at 25°C, where the  $\text{SiO}_2$  content of the solutions is over 9 ppm.

The significance of a chemical interaction between alumina and silica in solution is that a colloidal high free energy of formation product, -897 K.Cal/Mol., does form and provides the mechanism for removal of  $\text{SiO}_2$  even at pH 10. Figure 12.

Many workers have noted the special insolubilizing effect of aluminum ion on silica<sup>34</sup> in various applications, such as suppression of the quartz reaction with lung tissue which causes silicosis. Iler<sup>35</sup> showed that alumina adsorbed on the surface of amorphous silica reduces the rate of solution, as well as the equilibrium solubility, of silica in water, even when less than a monolayer of  $\text{Al}^{+++}$  ions is present.

Millot<sup>36</sup> (particularly p. 349 et seq.) has given a convincing explanation of the dynamics of clay formation.

In general, feldspar can be converted, under somewhat acidic leaching conditions (complexing acids, humic acids,  $\text{CO}_2$ , or mineral acids), to a series of compounds with accompanying elimination of  $\text{Si(OH)}_4$ .



The kaolinite formed can, in turn, be leached to yield gibbsite,  $\text{Al(OH)}_3$ . But, the important point is that these reactions are reversible and that clay minerals can be formed from silica and alumina, given appropriate cation concentrations (Pedro, in Millot).<sup>36</sup> Generally, in the presence of excess alumina (in alumina-silica gels) the hexacoordinate form of alumina is favored at pH's from 4.5 or 5.0 to 8. This fact is significant because of its possible favorable effect on the removal of silica from water.

Summarizing the optimum conditions for clay formation (Millot<sup>36</sup> p. 344) states that:

1. An increase in the relative concentration of alumina in a "gel" favors the hexacoordinate form of aluminum.
2. Low pH favors hexacoordination of  $\text{Al}^{+++}$  also.
3. Decreasing the electrolyte content tends to promote hexacoordination and hence the formation of kaolinite.
4. The presence in the gel of crystalline nuclei of gibbsite is necessary for development of kaolinite.

Referring to Wey and Siffert's<sup>10</sup> work, Millot (pp. 420-425) states that

because the solubility of alumina is approximately 1 ppm, it can adsorb silica, whose solubility is about 120-140 ppm. Alumina can, therefore, fix silica onto the layered gibbsite structure.

The curves in Fig. 13, after Wey and Siffert (Millet, p. 350), show the solubility of silica from clays. Compared to the solubility of amorphous  $\text{SiO}_2$ , kaolinite exhibits negligible silica solubility.

#### METHODS FOR REMOVING SILICA FROM WATER

##### Alumina

The preceding discussion has dealt mainly with the geochemical aspects of the interaction of alumina with silica. However, the practical effect of alumina in removing silica from water is well known.<sup>37-39</sup> Behrman<sup>37</sup> and the others,<sup>38,39</sup> have all shown the potential of aluminum ion for removing silica from water with alumina in some form. Behrman et al. mentioned, in passing, one water's silica-content reduction from 68 to 5 ppm by passage through a bed of alumina. They mention many "favorable results" without giving details.

Lindsay and Ryznar<sup>38</sup> used sodium aluminate in solution to remove silica from water. They found that they could remove a "substantial proportion" of silica from waters containing 3.3 to 95.2 ppm by using weight ratios of 1:5 sodium aluminate:silica. The results showed that maximum removal occurred at pH 8-9. The treatment was a flocculation type involving recycling of a preformed sludge. The treatment added appreciable lime and sodium to the water. Incidentally, on a simple weight basis, a comparison with ferric sulfate showed the aluminate to be more than twice as effective as the former for removing silica.

The best treatment for a water containing 95.2 ppm of  $\text{SiO}_2$  consisted of 255 ppm of sodium aluminate (90%) and 4.5 ppm of lime with HCl added to pH

adjustment. Residual silica was 2.8 ppm. Ferric sulfate under similar conditions left 47 ppm of silica. Doubling the ferric sulfate and lime left 20 ppm of  $\text{SiO}_2$  in solution.

Wey and Siffert,<sup>10</sup> Fig. 14, starting with 140 ppm of monomeric silica in solution and 42 ppm of  $\text{Al}^{+++}$ , left as much as 70 ppm of  $\text{SiO}_2$  in solution (in the absence of NaCl) at 8-10 pH. In the presence of NaCl, there was about 20 ppm of soluble silica left in solution. On a 1:1 molar basis, there should have been about 57 ppm left.

The effect of "some NaCl" on the removal of silica from solution by  $\text{Al}^{+++}$  indicates that a colloid had formed and was being flocculated out. This is probably an ionic strength effect. Stumm and O'Melia<sup>26</sup> have discussed the conditions for mutual coagulation of alumina and silica in detail.

Apparently little commercial use has been made of either  $\text{Fe}^{3+}$  or  $\text{Al}^3$  as flocculants for the removal of silica from solution, possibly because of the disadvantages inherent in the flocculation process together with the poor removal in most cases. It is also true that in most parts of the country, silica is not present in concentrations of over 40 ppm in river water; usually less than 30 ppm in lake waters and less than 30 ppm in spring waters (Ref. 40, pp. 19-28). These are sufficiently low for most cooling waters; for steam generation the use of magnesia and later ion exchange resins for silica removal were apparently more advantageous.

Liebknecht<sup>41</sup> patented the use of dried (80-90°C) hydrous oxide gels such as those of iron, aluminum, titanium, chromium, cerium, scandium, magnesium, copper, tin, zirconium, thorium, and tungstic acid as column adsorbents for  $\text{SiO}_2$ .

#### Iron

We have cited some results with ferric sulfate as a flocculation agent under "Alumina." Liebknecht<sup>41</sup> using iron oxide as an example, found that at



the rate of 0.5 column volume per minute, the silica in a 17-ppm  $\text{SiO}_2$  water was reduced to 1 ppm. After the passage of 1600 column volumes of the water, there was still enough capacity left to reduce the silica content to 7-9 ppm. Apparently, little or no commercial use has been made of the process.

Schwartz<sup>42</sup> reviewed the removal of silica with ferric hydroxide from water for boiler feed purposes in 1938. A pH at about pH 9.0 has been used for silica removal. The dosage required, up to 20 ppm (Ref. 40, pp. 387-388), is a function of silica content. The sulfate content is increased so that if the water is subsequently softened, removal of 1 ppm of  $\text{SiO}_2$  would cause addition of 8.5-21 ppm of sodium sulfate. Its usefulness in silica removal is now mainly as a coagulant aid for magnesia (Ref. 40, p. 513). Leaf,<sup>43</sup> using water very similar to Los Alamos water, found that fresh iron oxide, formed by the rusting of iron in situ, in a column was a "very good" adsorbent for silica. The difficulties of producing such fresh rust and the eventual cementing of the iron shavings caused the project to be abandoned.

#### Magnesium

Other than anion resins, magnesium ion has been the agent most used to remove silica from water. This is one of the few species that react specifically with  $\text{Si}(\text{OH})_4$ . Magnesia is well known for its presence in clays and also for its hexacoordinate structure in the form of brucite. (This is in line with the previous discussion indicating the importance of hexacoordination for the polymerization of silica.)

The insolubility of at least one magnesium silicate, sepiolite, has already been discussed (Clay Formation).

Way and Siffert<sup>10</sup> (Fig. 15) showed that for a saturated amorphous  $\text{SiO}_2$  solution with about 140 ppm silica content, with an equivalent amount of added  $\text{MgCl}_2$ , the maximum precipitation is at pH 11-11.5. About 35 ppm of

$\text{SiO}_2$  remains in solution. The region of  $\text{Mg}(\text{OH})_2$  insolubility is from pH 9.2 upwards.

Betz et al<sup>39</sup> have shown that addition of 100 ppm of "active" MgO can reduce the silica content at 93°C from 22 to 1 ppm. However, at 30°C the reduction is only to 16 ppm. The efficiency of removal is very much a function of temperature. The  $\text{Mg}(\text{OH})_2$  has an inverse coefficient of solubility, so that, in practice, higher temperatures reduce the hardness. The hardness in this case goes from 88 to 28. The original hardness was 36.

A common method of water "softening" is the hot-lime process in which lime (or dolomitic lime) and soda ash are added to water preheated with steam. Such a system is often used to remove silica.

Figure 16, (Nordell,<sup>40</sup> p. 513) shows the marked effect of temperature on silica removal as a function of silica:magnesium ratio.

A very practical set of curves from Nordell<sup>44</sup> (Fig.17), shows the relation between silica percent and magnesia added for removal. These curves include a 15% safety factor. The disadvantages of the process are:

1. For good silica removal, the process must be operated hot.
2. It requires recirculation of sludge and cold influent for maximum reaction with silica.
3. Cost - the  $4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  costs 16-22¢/lb.

## EXPERIMENTAL

The experimental program was preliminary and semiquantitative; designed mainly for orientation as to technique.

### Test of an Active Alumina's Capacity as an $\text{SiO}_2$ Adsorbent

We made up a 20-ml volume column of an active alumina in a Pyrex tube with

a coarse, fritted disk seal. The alumina was Amerd Chemical Company's 80-200 mesh, "chromatographic grade." Tap water was passed through at 4-6 ml/min. The vessels were Pyrex, and we did not try to account for the solubility of the silica from the glass. The silica content of the effluent water was determined by standard molybdate colorimetric methods for monomeric (or active silica).<sup>45</sup> The first three column volumes of filtrate were discarded. Measurements were made on subsequent increments.

Table I shows the results. Data from the single set of results indicate an "induction period" when 200-250 ml of water passed through the column, during which removal was not complete. Silica was practically completely removed from the water during passage of 250 column volumes of water. After passage of 830 column volumes, about 50 ppm of silica, out of 80, was still being removed. After filtration of 1400 column volumes, there was still a reduction in silica content.

#### Beaker Tests for Silica Flocculation

Adsorption on Alumina of  $\text{SiO}_2$  from Los Alamos Tower Water. This was a test to determine whether alumina, in a "stirred" beaker test, would affect the silica content of a more concentrated (146 ppm  $\text{SiO}_2$ ) water from the Los Alamos No. 3 cooling tower. We added various weight ratios ( $\text{Al}_2\text{O}_3:\text{SiO}_2$ ) of "chromatographic grade" alumina to the water samples and stirred them for 2 h at about 70 rpm. The clarified water was filtered.

Table II shows that the 1:1 weight, ratio  $\text{Al}_2\text{O}_3:\text{SiO}_2$  seemed to have little effect on the silica. Doubling the ratio removed about 30% of the silica. Further increases had little effect on removal. Perhaps what was being removed was a colloidal or higher polymer, and only a slight or slow interaction occurred between the dissolved silica and the  $\text{Al}_2\text{O}_3$ .

## Adsorption of $\text{SiO}_2$ on Magnesium Hydroxide

We made three sets of tests under different conditions.

1. In this test we used magnesium sulfate solution, made alkaline with additions of lime, as the source of magnesia to remove silica from water (80 ppm  $\text{SiO}_2$ ) at room temperature. These solutions were stirred at 100 rpm during mixing and at 30 rpm for 2 h. We added various equivalents of  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$  as shown in Table III. Twenty ppm of commercial grade ferric sulfate was used as a coagulation aid.

Table III shows that the silica is, indeed, reduced 85-88% under the test conditions, but with increased calcium hardness. Furthermore, the efficiency on the basis of  $\text{Mg}^{++}$  added is 64% at best. Probably 45-50% would be more common. Of course, this could be increased by hot operation.

2. Table IV shows the results of a test with LAMPF tower water concentrated to 150 ppm of  $\text{SiO}_2$ . We used magnesium-to- $\text{SiO}_2$  equivalents of less than 1. The results indicate that usually less than half of the silica present was removed. However, the efficiency of silica removal ranged from 60 to 115%. This probably indicates that the  $\text{SiO}_2$  was somewhat polymerized and was being removed rather readily. In fact the high efficiency for low  $\text{Mg}:\text{SiO}_2$  ratios may indicate that we were seeing a preferential removal of higher polymeric fractions.

3. Table X shows somewhat similar results when the source of  $\text{Mg}^{++}$  was a basic carbonate of magnesium. The water contained 240 ppm of  $\text{SiO}_2$ . This was tap water concentrated by evaporation to simulate the silica levels present at the Power Plant. At the low equivalents of added magnesium ion, the efficiency was well over 1. As the  $\text{Mg}^{++}:\text{SiO}_2$  ratio was increased, the efficiency dropped. It would be useful to determine whether this is truly a function of

the prior degree of polymerization or the effect of decreasing concentration on polymerization rate (Kitahara's equation).

#### The Treatment of Cooling Tower Blowdown with Electrochemically Generated Metal Hydroxides

There have been laboratory studies on the use of electrochemically generated ferrous hydroxide for the removal of chromate<sup>46</sup> and phosphate<sup>47</sup> from cooling tower blowdown and waste waters. A commercial unit is now available for the removal of chromate from cooling tower blowdown by the use of electrochemically generated ferrous hydroxide.<sup>49</sup> It has been shown also that electrolysis with Al electrodes could be used to remove  $\text{Na}_2\text{SiO}_3$  which had been added to river water.<sup>49</sup>

Since dissolved  $\text{SiO}_2$  in the water supply limits the number of cycles at which Los Alamos cooling towers can be operated,<sup>50</sup> a possible process for its removal seemed worthy of investigation. The treatment of cooling tower blowdown for which the makeup water was mostly secondary sewage<sup>46</sup> will be described.

Batch electrolyses were carried out with 2-liter samples of the cooling tower blowdown as previously described,<sup>46,47</sup> except in this study a variety of metals were evaluated in addition to the iron. These results are given in Table VI. The waters were electrolyzed with the given metal as both electrodes at a constant current of 1.0 amp and a variable potential of from 3 to 10 volts. The initial pH of the solutions was 8.6 and as the electrolysis proceeded the pH increased to 8.9 for the Al and to 10.7 for the Mg with the other metals falling between these limits.

As is seen in Table VI, Al appears to provide the best treatment. Since Al also results in the least change in the pH of the solution, preliminary studies of the possible recycle of the cooling tower blowdown have concentrated on the use of Al electrodes.

It is confirmed in Table VII that electrochemically generated Al is more effective than the same quantity of Al added as  $\text{Al}_2(\text{SO}_4)_3$  at the same final pH. In addition the electrochemically generated Al reduces the total dissolved solids (TDS) in the solutions while treatment with  $\text{Al}_2(\text{SO}_4)_3$  causes an increase in the TDS.

The pH of the Los Alamos cooling tower blowdown water before treatment was 8.6. In Table VIII the initial pH was adjusted to pH 5.5 before electrolysis and resulted in poorer removals of  $\text{SiO}_2$ , Ca, Mg, and TDS than when the initial pH was 8.6. These results are consistent with previous chemical coagulation studies for the removal of  $\text{SiO}_2$  from water.<sup>50</sup>

The continuous flow treatment unit previously described by Onstott et al.<sup>46</sup> was modified to use Al electrodes and was used to treat up to one gallon per minute of cooling tower blowdown. Preliminary results indicate that about 7.2 MJ (1/4 kWh) of direct current electricity and 0.2 Kg (one half pound) of Al electrode was needed to reduce the  $\text{SiO}_2$  content of  $3.8 \text{ m}^3$  (1000 gallons) of the water by 85%. This relatively high energy use should be compared with such alternative processes for recycle of water as evaporation, electrodialysis, ion exchange or reverse osmosis.

#### SUMMARY AND CONCLUSIONS

This review and discussion serves as a guide to our future work on the problem of silica deposition from water in heat exchangers.

The conclusions to be drawn are that silica in water is a metastable system whose behavior is difficult to predict. It tends to supersaturate and depending on other ions present, it precipitates. The solubility of silica is a function of the species with which it is in equilibrium. Silica shows incongruent solubility from various silicate species (such as clays).

Amorphous silica shows about 140 ppm solubility. The effect of pH on regions of stability have been worked out previously. However, rate data on polymerization are unavailable and data on the various species present in supersaturated solutions are scarce. In spite of low degree of ionization, silica does react with other ions and hydrous oxide species containing aluminum, magnesium, and iron. Experimental data as well as calculations of equilibria leading to simple clay type materials and to magnesium silicates are available. The data cited indicate that the magnesium and aluminum ions play a large role in natural systems in removing silica from water. These ions probably also have a large role in the deposition of silica in heat exchangers, judging from their presence in siliceous deposits. Additionally, these ions have been the basis for some commercial methods of  $\text{SiO}_2$  removal from water.

The experimental work described shows the superior usefulness of  $\text{Al}^{+++}$  for the removal of Silica from cooling waters.

Work is needed additionally on: (1) Determination of the factors and materials that influence the "supersaturation" of silica for extended periods; (2) further studies on removal of silica from waters by use of alumina as an adsorbent and on methods of regeneration; (3) detailed studies on removal by ion exchangers as compared with removal by alumina adsorbents; (4) Engineering studies on the influence of degree of supersaturation, presence of second phase, heat transfer rate, turbulence, etc., on the deposition of silica from cooling waters.

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## APPENDIX

Table IX shows analyses of scales and tuffs. The deposits showed only amorphous silica by "X-ray diffraction." The two tuffs showed alpha quartz, tridymite, alpha cristobalite and some amorphous constituents. The deposits were water derived, the  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were from components in the system. The analyses are typical of the waters discussed above. Table X shows some typical analyses for water.

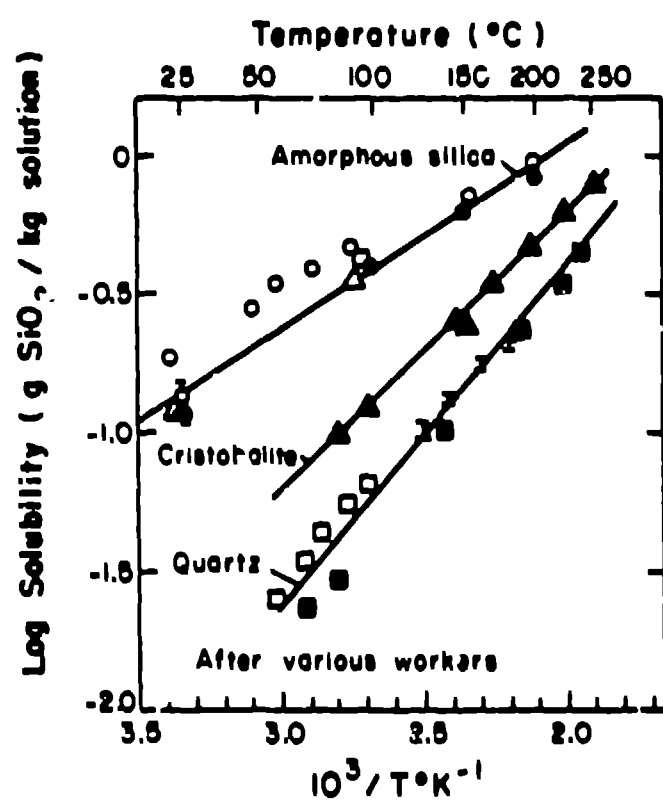
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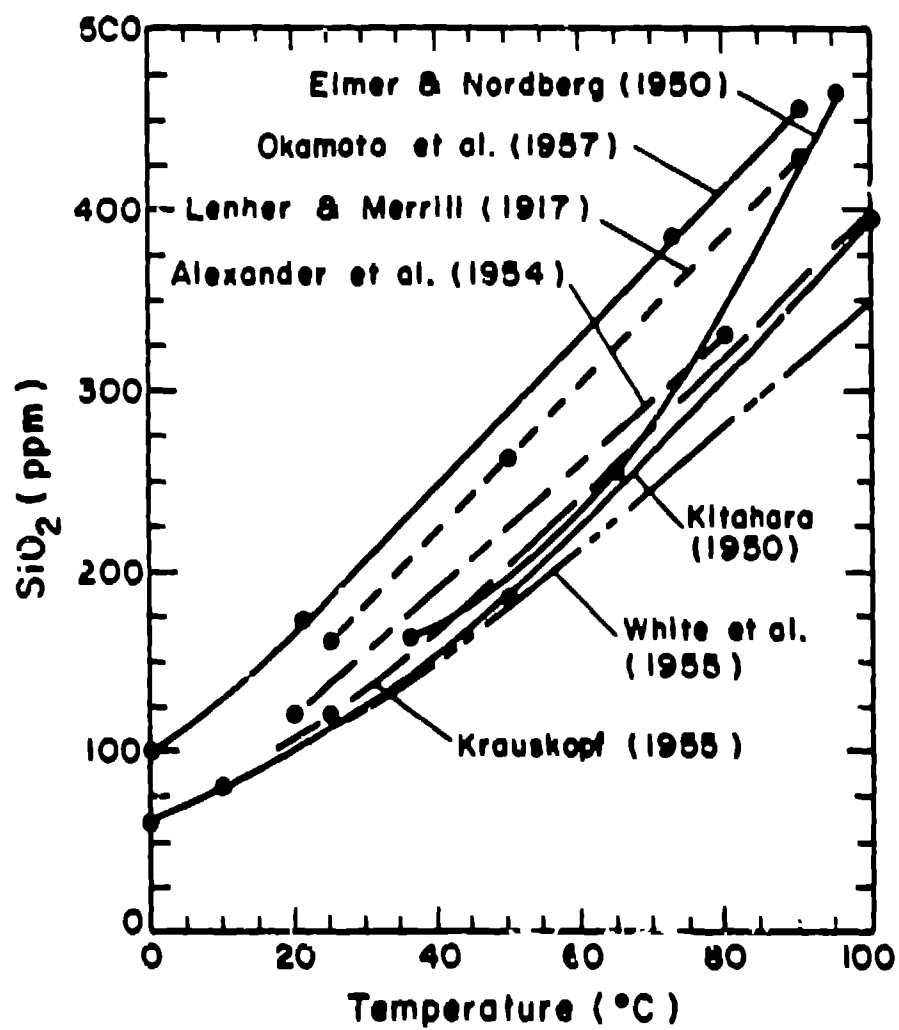
- Fig. 1. Solubility of quartz, cristobalite, and amorphous silica in water at 25-250°C.
- Fig. 2. Solubility of amorphous silica in water at 0-100°C. Curves plotted from the results of the indicated workers.<sup>3</sup>
- Fig. 3. Solubility of silica as a function of time.<sup>3</sup>
- Fig. 4. Solubility of silica in water: from sols made by removal of  $\text{Na}^+$  from sodium silicate solution and from suspensions of "Silica I," pH adjusted with HCl or NaOH.<sup>5</sup>
- Fig. 5. Change in colorimetric silica in hot-spring waters from Yellowstone National Park, Wyoming. Vertical lines join the results for individual water samples. The pH values were measured after the water had cooled to room temperature (the average temperature of the waters since collection was 25°C.).<sup>3</sup>
- Fig. 6. Solubility of amorphous silica, opal, cristobalite, and quartz (after Wey and Siffert).<sup>10</sup>
- Fig. 7. Species in equilibrium with amorphous silica. Adapted from Stumm et al.<sup>18</sup>
- Fig. 8. The influence of pH and silica concentration on sol stability. Adapted from R. C. Ray and P. B. Ganguly.<sup>23</sup>
- Fig. 9. Precipitation of colloidal silica.  $\text{SiO}_2$ , 45 mg/liter; Al, 1 mg/liter.<sup>25</sup>
- Fig. 10. Precipitation of molecularly dispersed silica.<sup>25</sup>
- Fig. 11. Precipitation of colloidal silica at various aluminum concentrations.<sup>25</sup>  
 A.  $\text{SiO}_2$ , 92 mg/liter; Al, 1 mg/liter.  
 B.  $\text{SiO}_2$ , 92 mg/liter; Al, 2 mg/liter.  
 C.  $\text{SiO}_2$ , 43 mg/liter; Al, 0.5 mg/liter.
- Fig. 12. Stability fields of synthetic halloysite and microcrystalline gibbsite and solubility of aluminum as functions of pH and activity of undissociated aqueous silica at 25°C and 1 atmosphere. Ionic strength 0.01. After J. D. Hem et al.<sup>33</sup>
- Fig. 13. Solubility of the silica of various clays, after Wey and Siffert.<sup>10</sup>
- Fig. 14. Removal of  $\text{SiO}_2$  from a saturated (140 ppm) solution by  $\text{Al}^{3+}$  as a function of pH.<sup>11</sup>

Fig. 15. Removal of  $\text{SiO}_2$  from a saturated (140 ppm) solution by  $\text{Mg}^{2+}$  (sulfate) as a function of pH.<sup>10</sup>

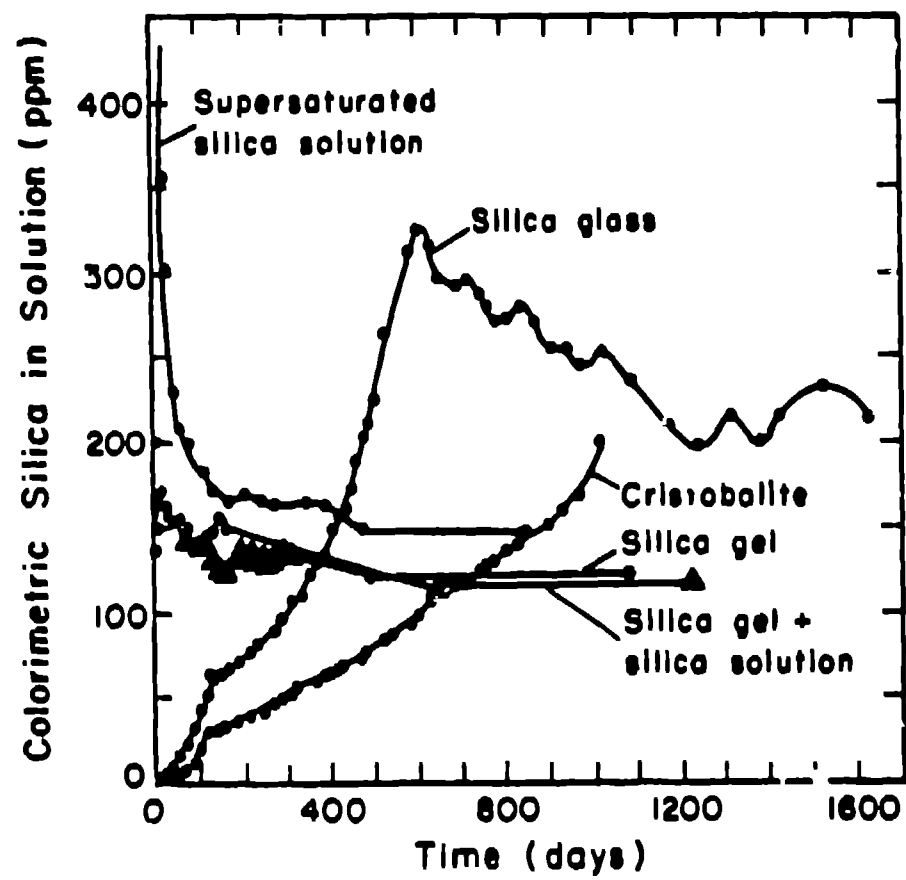
Fig. 16. Temperature effects on silica removal by magnesium hydroxide.<sup>38</sup>

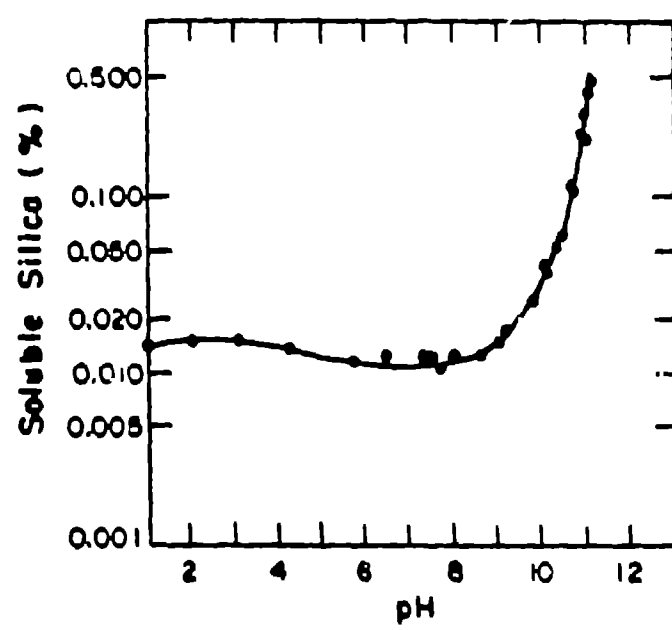
Fig. 17. Silica removal by magnesia in hot lime-soda process.<sup>44</sup>

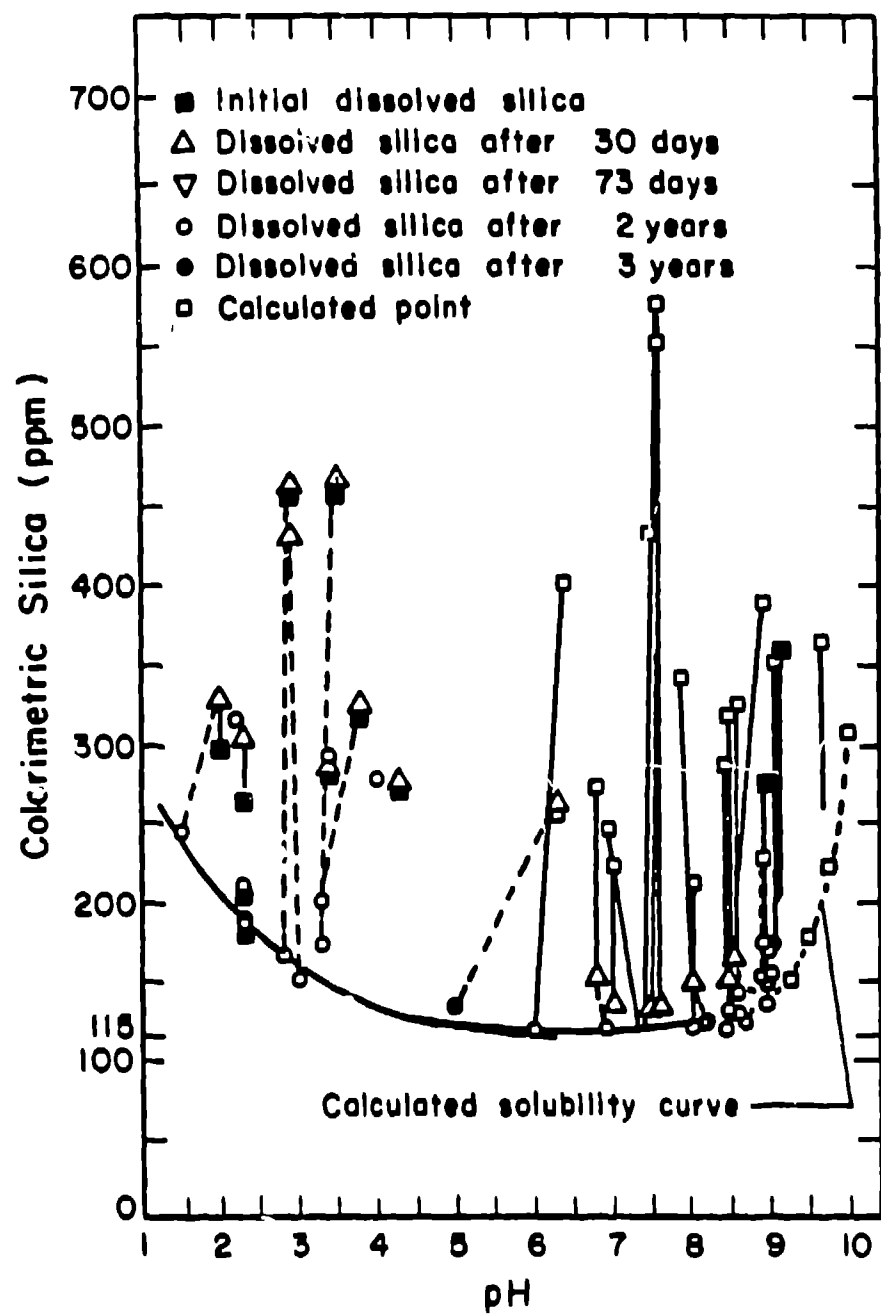


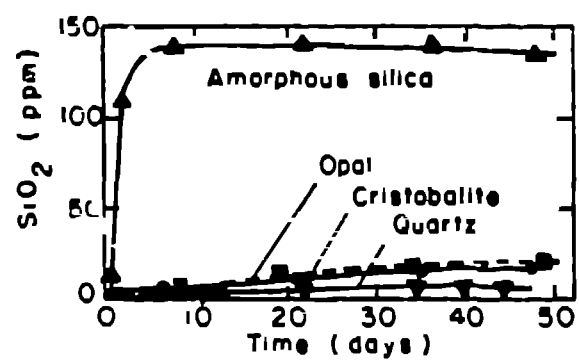












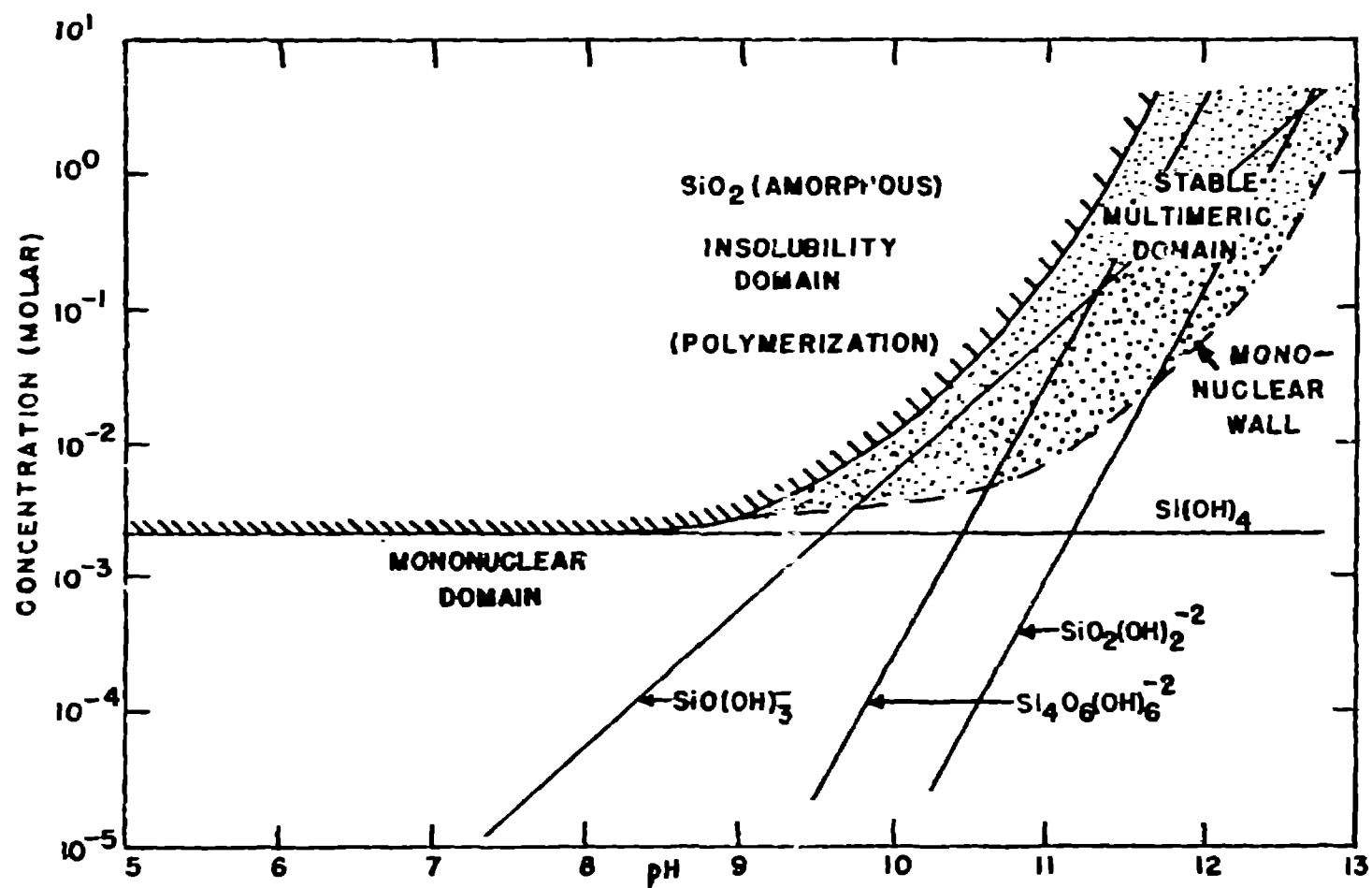
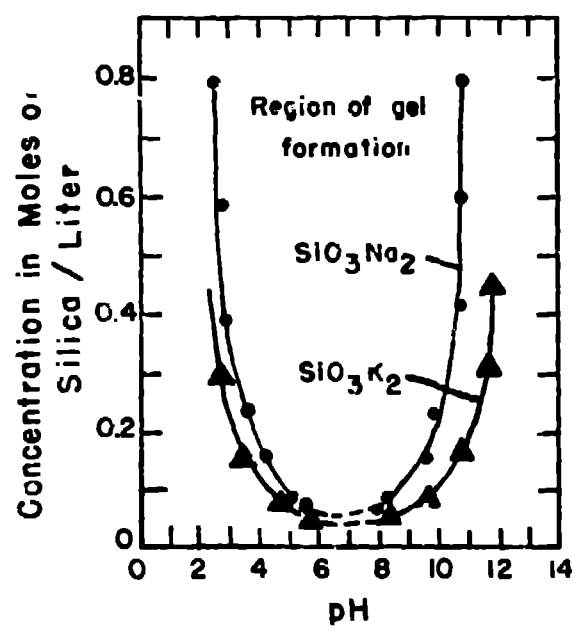
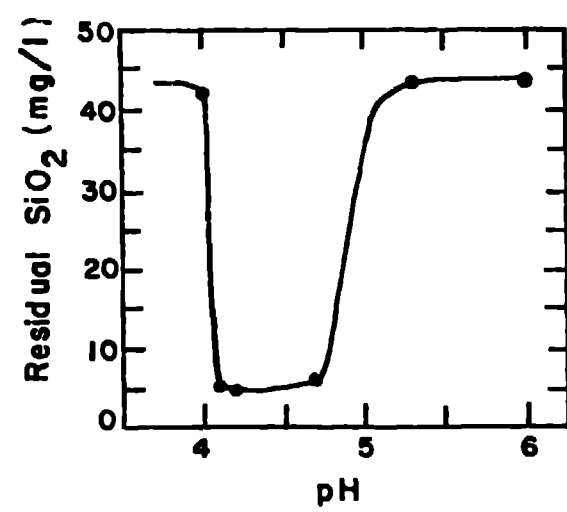
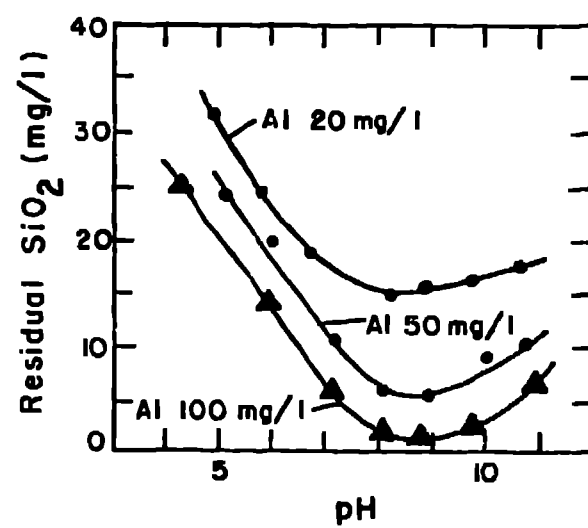


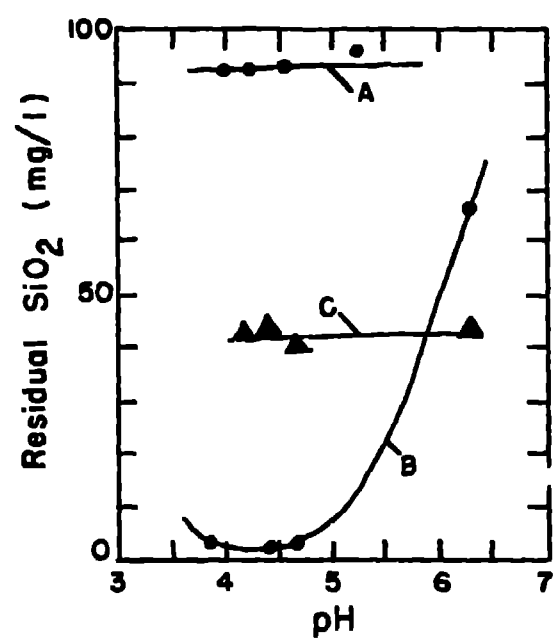
Figure . Species in equilibrium with amorphous silica











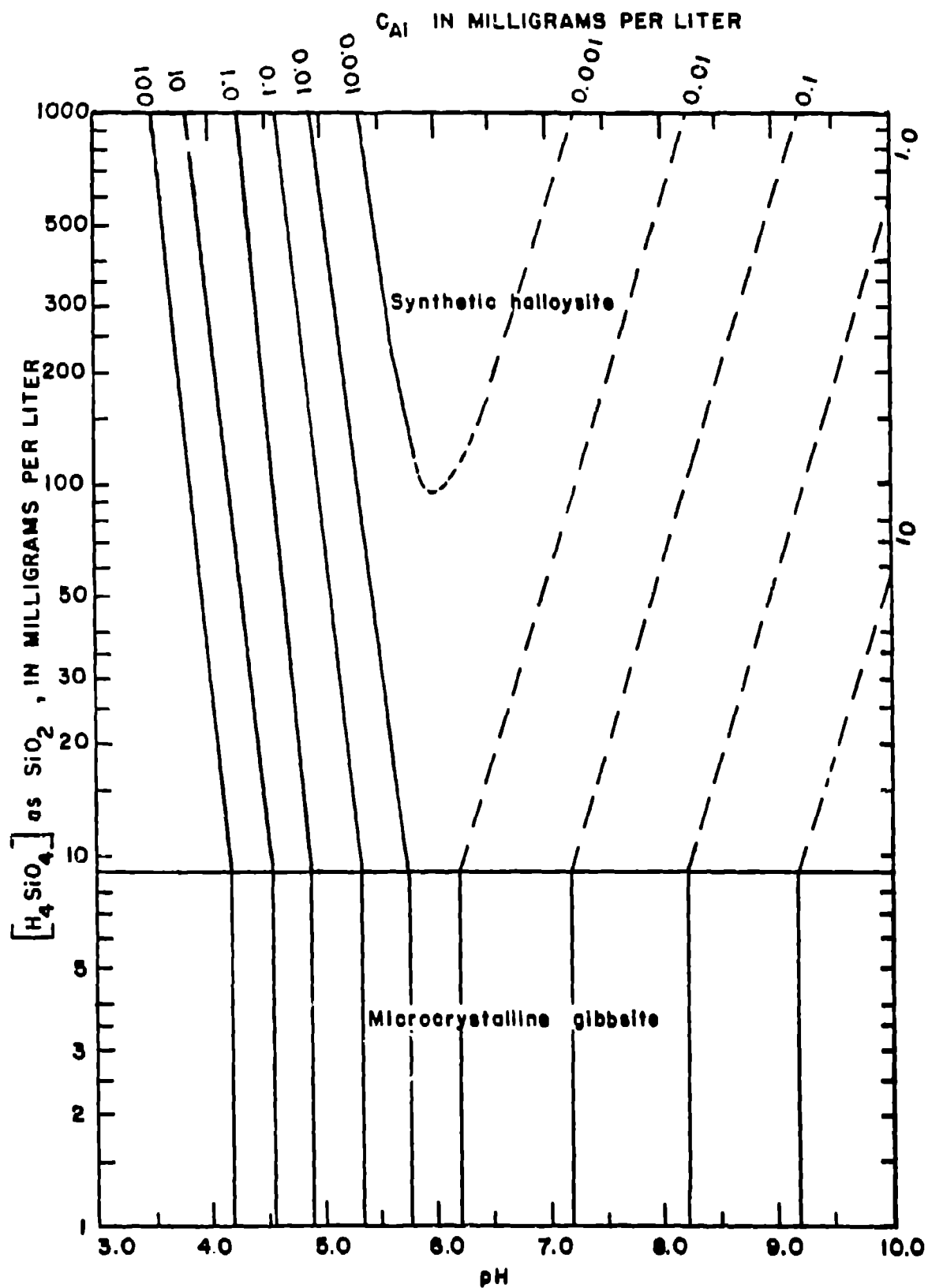
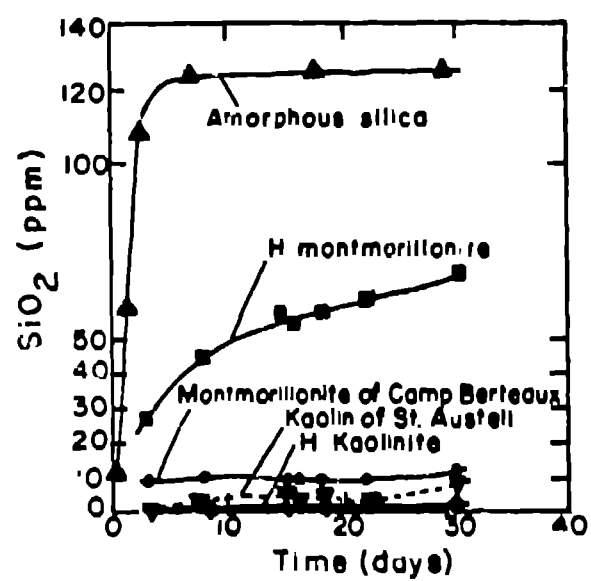
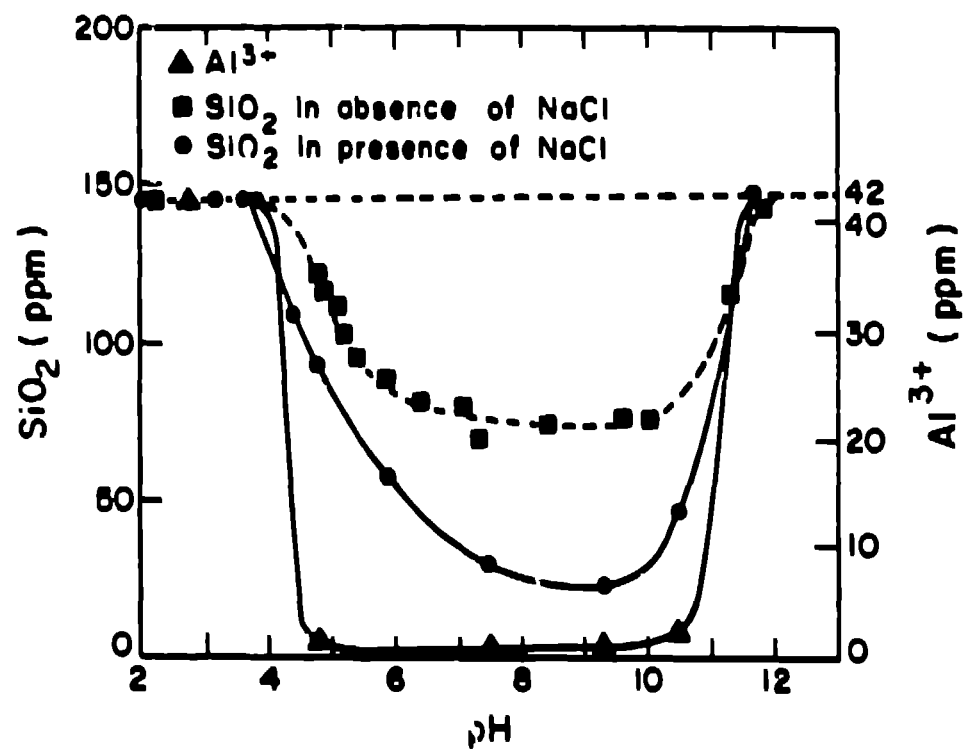
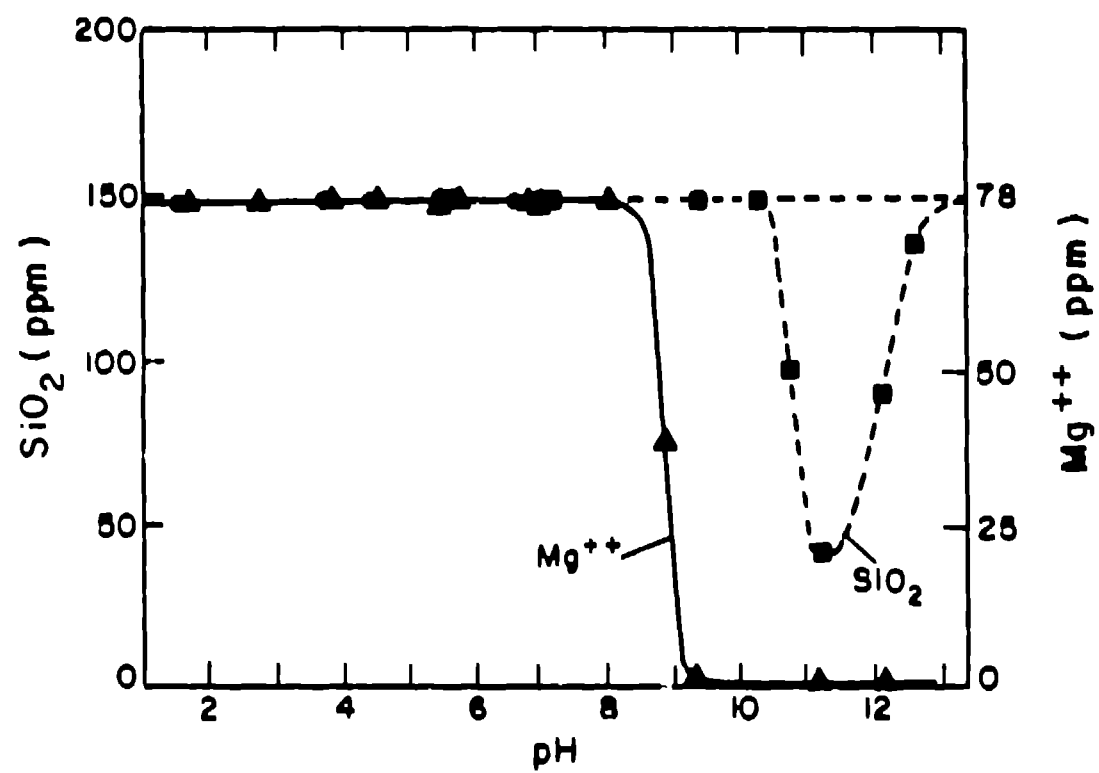
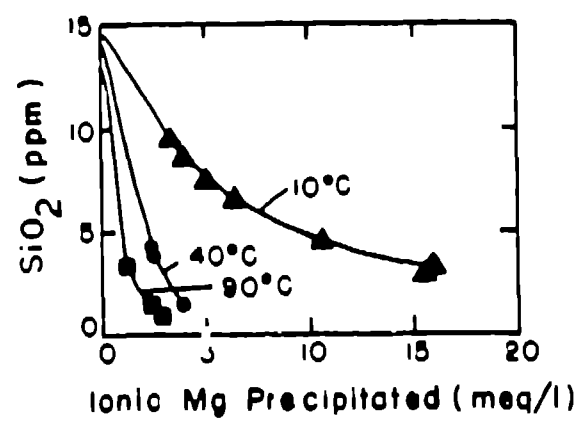


Figure . Stability fields of synthetic halloysite and microcrystalline gibbsite and solubility of aluminum as functions of pH and activity of undissociated aqueous silica at 25°C and 1 atmosphere. Ionic strength 0.01









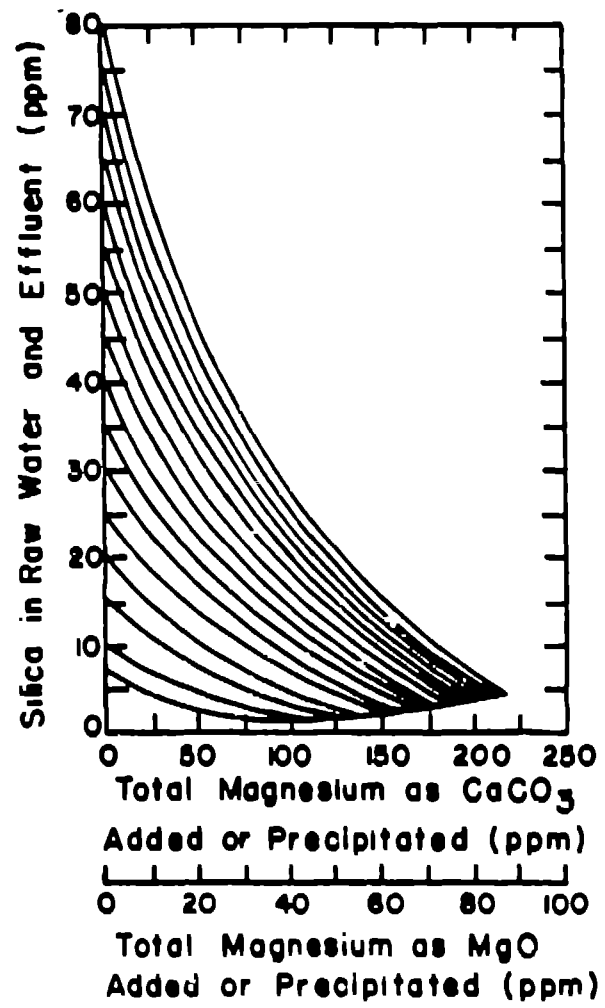


TABLE I

REMOVAL OF SILICA FROM TAP WATER BY AN ALUMINA COLUMN<sup>a</sup>

Collected Throughput (ml)	No. of Column Volumes of Water Throughput	Analysis			
		SiO <sub>2</sub> (ppm)	Ca <sup>++</sup> (ppm)	Mg <sup>++</sup> (ppm)	pH
Tap-water control	-	82	12	4	8.3
0-125	6	3	-	-	-
150-250	12	16	4	-	-
350-450	22	0.4	0	-	8.3
650-750	37	0	0	0	8.3
1100-1200	60	0	2	0	7.6
1800-1930	96	0	-	-	7.6
1930-2030	101	0	-	-	-
2752-2850	142	0	0	0	7.5-8.0
4850-4950	247	6	0	0	-
16650	832	30	11	4	-
17300	865	48	-	-	-
17670-22170	1108	53	-	-	7.5
27270-28370	1418	66	13	2	7.5

<sup>a</sup>Column: 20-ml alumina, 5.3-cm height. Alumina powder: 80-200 mesh chromatographic grade, Amend Drug and Chemical Co., New York.



TABLE II  
 ADSORPTION ON ALUMINA<sup>a</sup> OF SiO<sub>2</sub> FROM LAMPF WATER

<u>Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub></u>	<u>Analysis</u> <u>After Treatment</u>	
	<u>SiO<sub>2</sub></u> (ppm)	<u>pH</u>
LAMPF-water control	146	-
1:1	140	8.1
2:1	98	8.0
3:1	92	8.0
4:1	88	8.05
5:1	83	8.5

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<sup>a</sup>Alumina powder, 80-200 mesh, chromatographic grade, Amend Drug and Chemical Co., New York.

TABLE III

## BEAKER TEST

ADSORPTION ON MAGNESIA OF  $\text{SiO}_2$  FROM TAP WATER<sup>a</sup>

No.	Equiv <sup>b</sup> $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Equiv <sup>c</sup> $\text{Ca(OH)}_2$	Analysis				$\text{SiO}_2$ Equiv Found	$\text{SiO}_2$ Equiv Removed	Efficiency ( $\text{SiO}_2$ Equiv Removed/ $\text{Mg}^{++}$ Equiv Added)
			$\text{SiO}_2$ (ppm)	pH	$\text{Ca}^{++}$ (ppm)	$\text{Mg}^{++}$ (ppm)			
W-1	1	1 <sup>d</sup>	48	10.2	40	24	0.60	0.40	0.40
W-2	1	2	29	10.3	66	1.2	0.36	0.64	0.64
W-3	2	2	10	10.3	100	5.1	0.12	0.88	0.44
W-4	2	4	12	11.2	132	1.2	0.15	0.85	0.43
W-5	1	0	72	7.0	18	20.7	0.90	0.10	0.10
W-6	1	0	73	7.8	38	18.2	0.91	0.09	0.10

<sup>a</sup>80 ppm of  $\text{SiO}_2$  in water.

<sup>b</sup>To form metasilicate  $\text{MgO} \cdot \text{SiO}_2$ :  $\text{SiO}_2 + \text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Ca(OH)}_2 \longrightarrow \text{MgOSiO}_2 + \text{CaSO}_4$ .

<sup>c</sup>Commercial lime, about 90%  $\text{Ca(OH)}_2$ .

<sup>d</sup>20 ppm of commercial-grade ferric sulfate as a flocculant, room temperature, stirred at 100 rpm during mixing and 2 h at 30 rpm.

TABLE IV

## BEAKER TEST

ADSORPTION ON MAGNESIA OF  $\text{SiO}_2$  FROM TOWER WATER<sup>a</sup>

No.	Equiv <sup>b</sup> $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ Added	Equiv <sup>c</sup> $\text{Ca}(\text{OH})_2$ (to $\text{Mg}^{++}$ )	Analysis			Efficiency ( $\text{SiO}_2$ Equiv Removed/ $\text{Mg}^{++}$ Equiv Added)
			$\text{SiO}_2$ Found (ppm)	$\text{SiO}_2$ Equiv Found	$\text{SiO}_2$ Equiv Removed	
B-12	-	-	150	-	-	-
B-13	0.16	0.40	149	1.0	0	0
B-14	0.24	1.19	108	0.72	0.28	1.15
B-15	0.38	0.81	97	0.65	0.35	0.93
B-16	0.49	2.16	92	0.61	0.39	0.80
B-17	0.75	0.81	83	0.55	0.45	0.60
B-18	0.75	1.62	33	0.22	0.78	1.03

<sup>a</sup> $\text{SiO}_2$ , 150 ppm in LAMPF tower water.

<sup>b</sup> $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , laboratory reagent.

<sup>c</sup>Commercial lime, about 90%  $\text{Ca}(\text{OH})_2$ .

TABLE V  
REMOVAL OF  $\text{SiO}_2$  FROM CONCENTRATED TAP WATER  
BY BASIC MAGNESIUM CARBONATE<sup>a</sup>

No.	<u>Equiv Mg<sup>++b</sup></u>	<u>Equiv Ca(OH)<sub>2</sub> to Mg<sup>++</sup></u>	<u>SiO<sub>2</sub> Found (ppm)</u>	<u>SiO<sub>2</sub> Equiv Found</u>	<u>SiO<sub>2</sub> Equiv Removed</u>	<u>Eff<sup>c</sup></u>
B-1	0.21	0.21	175	0.73	0.27	1.30
B-2	0.42	0.42	154	0.64	0.36	0.86
B-3	1.00	1.00	138	0.57	0.42	0.43
B-4	1.40	1.50	116	0.48	0.52	0.37
B-0	-	-	240	-	-	-

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<sup>a</sup>  $4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  Mallinckrodt analytical reagent.

<sup>b</sup>  $4 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 4\text{Ca}(\text{OH})_2 + 5 \text{SiO}_2 = 5 \text{MgSiO}_3 + 4 \text{CaCO}_3$ .

<sup>c</sup> Efficiency =  $\frac{\text{SiO}_2 \text{ eq removed}}{\text{Mg}^{++} \text{ eq added}}$  .

TABLE VI

THE EFFECT OF ELECTROCHEMICALLY GENERATED METAL HYDROXIDES  
ON SILICA, CALCIUM, MAGNESIUM AND TOTAL DISSOLVED SOLIDS  
IN LOS ALAMOS COOLING TOWER BLOWDOWN

Metal	Time of Electrolysis at 1.0 Amp								
	10 minutes			20 minutes			30 minutes		
	SiO <sub>2</sub>	Ca & Mg	TDS	SiO <sub>2</sub>	Ca & Mg	TDS	SiO <sub>2</sub>	Ca & Mg	TDS
Al	73	11 - 6	536	9	8 - 4	368	1	5 - 1	336
Cu	119	22 - 8	610	103	20 - 8	579	90	19 - 7	551
Fe	115	14 - 7	672	41	10 - 5	520	17	11 - 4	440
Mg	135	21 - 28	782	84	18 - 32	716	36	21 - 25	566
Zn	117	26 - 10	650	67	24 - 9	718	32	24 - 15	680

All results are given in mg/l.

The concentrations before electrolysis were: SiO<sub>2</sub> = 160 mg/l, Ca = 24 mg/l, Mg = 9 mg/l and TDS = 634 mg/l.

TABLE VII

A COMPARISON OF THE EFFECTIVENESS OF ELECTROCHEMICALLY GENERATED ALUMINUM WITH THE SAME QUANTITY OF ALUMINUM SUPPLIED BY  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  ON THE  $\text{SiO}_2$ , Ca, Mg, AND TDS FROM LOS ALAMOS COOLING TOWER BLOWDOWN

	85 mg/l Al		170 mg/l Al		255 mg/l Al	
	<u>Electro.</u>	<u><math>\text{Al}_2(\text{SO}_4)_3</math></u>	<u>Electro.</u>	<u><math>\text{Al}_2(\text{SO}_4)_3</math></u>	<u>Electro.</u>	<u><math>\text{Al}_2(\text{SO}_4)_3</math></u>
$\text{SiO}_2$	73	110	9	48	1	5
Ca & Mg	11 - 6	22 - 7	8 - 4	18 - 6	6 - 1	14 - 3
TDS	536	852	368	1203	336	1602

All results are given in mg/l.

The concentrations before treatments were:  $\text{SiO}_2$  = 160 mg/l, Ca = 24 mg/l, Mg = 9mg/l and TDS = 634 mg/l.

TABLE VIII

THE EFFECT OF INITIAL pH ON THE TREATMENT  
OF LOS ALAMOS COOLING TOWER BLOWDOWN BY ELECTROCHEMICALLY  
GENERATED ALUMINUM HYDROXIDE

	Time of Electrolysis at 1.0 Amp					
	10 minutes		20 minutes		30 minutes	
	pH 8.6	pH 5.5	pH 8.6	pH 5.5	pH 8.6	pH 5.5
SiO <sub>2</sub>	73	97	9	37	1	16
Ca & Mg	11 - 7	26 - 6	8 - 4	22 - 6	6 - 1	22 - 6
TDS	536	714	368	628	336	534

All results are given in mg/l.

The concentrations before electrolysis were: SiO<sub>2</sub> = 160 mg/l,

Ca = 24 mg/l, Mg = 9 mg/l and TDS = 634 mg/l.

TABLE IX

ANALYSES OF SCALES AND TUFF AS FOUND  
AT VARIOUS INSTALLATIONS AT LASL

Constituent	*Cooling Tower % Deposit ETL Bldg.	SM-40 Scale	**Chiller # 2 E. Sec. LAMPF	Local Tuff	
				Sample I	Sample II
SiO <sub>2</sub>	61.3	42.6	56.5	81.0	66.1
Fe <sub>2</sub> O <sub>3</sub>	5.6	-	10.3	1.9	1.0
Al <sub>2</sub> O <sub>3</sub>	1.8	-	0.5	7.7	10.0
CaO	8.9	5.7	0.5	0.4	1.1
MgO	0.4	1.2	0.5	none	none
Na <sub>2</sub> O	1.0	-	-	2.1	3.9
CuC	none	-	-	none	none
ZnO	none	-	-	none	none
P <sub>2</sub> O <sub>5</sub>	2.7	-	-	0.1	Tr
CO <sub>2</sub>	4.0	-	-	none	none
Loss on Ignition	10.2	-	23.9	0.4	0.8
Undetermined	4.0	-	7.7	6.1	16.3

\*Data from Ebasco Services, Inc. report November 30, 1973, quoted from Phoenix Company report, samples collected August and September 1970.

\*\*Data from Pomeroy and Thomas, August 7, 1973.



Miscellaneous Data

TABLE X

ANALYSES OF TAP WATER (TA-50, LASL)

	<u>Sampled, mg/ml</u>	
	<u>8/16/73</u>	<u>10/29/73</u>
pH	7.9	7.9
Conductivity	124	110
P. Alk. ( $\text{CaCO}_3$ )	0	0
Total Alk. ( $\text{CaCO}_3$ )	64	60
Total Hardness ( $\text{CaCO}_3$ )	48	40
Calcium ( $\text{Ca}^{++}$ )	13	13
Magnesium ( $\text{Mg}^{++}$ )	4	2
Sodium ( $\text{Na}^+$ )	11	9
Chloride ( $\text{Cl}^-$ )	6	4
Fluoride ( $\text{F}^-$ )	0.2	0.2
Nitrate Nitrogen (N)	0.2	0.2
Silica ( $\text{SiO}_2$ )	80	82
Total Solids	156	176